

1.043.485



## PATENT SPECIFICATION

NO DRAWINGS

1.043.485

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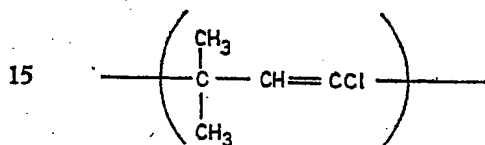
## COMPLETE SPECIFICATION

## Polymers containing Unsaturated Linkages

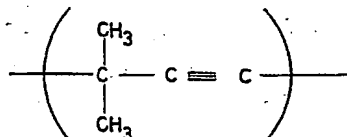
We, W. R. GRACE & CO., a Corporation organised and existing under the laws of the State of Connecticut, United States of America, of 7 Hanover Square, New York 5, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new polymers and to their production.

In one aspect this invention provides a linear polymer containing recurring structural units of the formulae:—



and



20 in the polymer chain, and having infrared absorption bands at  $970\text{ cm}^{-1}$ ,  $1300\text{ cm}^{-1}$  and  $2120\text{ cm}^{-1}$ . In its preferred form the polymer is benzene-soluble and has a softening point greater than  $360^\circ\text{C}$ . and a number average molecular weight between 500 and 10,000.

25 In a further aspect the invention provides a process for the preparation of the above polymer by polymerising 1,1 - dichloro - 2,2-dimethyl - cyclopropane in the presence as catalyst of a Friedel-Crafts catalyst at a temperature of  $20\text{--}100^\circ\text{C}$ . Preferably the weight ratio of the monomer to the Friedel-Crafts catalyst is between 100:1 and 1:1, and the

polymerisation is effected in the absence of a solvent, at atmospheric pressure and at ambient temperature. However, if desired the reaction can be carried out in an aromatic or saturated aliphatic hydrocarbon or chlorinated hydrocarbon solvent, e.g. benzene, hexane, heptane, or methyl, ethyl or butyl chloride, and at either subatmospheric or superatmospheric pressures.

As used herein the term Friedel-Crafts catalyst means any Lewis Acid capable of initiating cationic, that is, carbonium ion type polymerisation. Examples of suitable Friedel-Crafts catalysts include but are not limited to  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{BF}_3$  and  $\text{SnCl}_4$ .

The monomer, 1,1 - dichloro - 2,2-dimethyl - cyclopropane, can be synthesised by the method of W. von E. Doering and W. A. Henderson, J.A.C.S., Vol. 80, pg. 5274 (1958). In the polymerisation of this monomer 1 or 2 molecules of  $\text{HCl}$  are eliminated for each mole of monomer to yield a non-cross-linked polymer. In view of the number of double and triple bonds present in the polymer it is surprising that the polymer is not cross-linked, but since it is completely soluble in cold benzene the amount of cross-linking (if any) must be very small.

The physical properties of the polymers were determined as follows: the softening point was measured on a Fisher Johns melting block; the number average molecular weight was measured on a Mechrolab Vapor Pressure Osmometer, Model 301—A manufactured by Mechrolab Inc., Mountain View, California in accord with the instructions therefor; and the infrared (I.R.) spectra were obtained with a Perkin-Elmer 21 I.R. Spectrometer using solid films of the polymer, 12.5 to 25 microns in thickness.

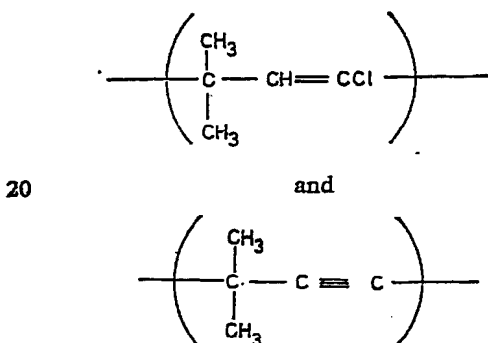
The following Examples illustrate the invention.

## EXAMPLE 1

10 g. of 1,1 - dichloro - 2,2 - dimethyl-cyclopropane were charged to an open beaker at room temperature ( $25^\circ\text{C}$ ). 1 g. of  $\text{AlCl}_3$  was added to the beaker and heat was evolved

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immediately with the formation of a black powder. The reaction was discontinued after 10 minutes and the reaction mixture was transferred to boiling methanol to dissolve out the catalyst. The powder product turned brown in the methanol. The product was filtered free of methanol and dried. The resulting dried polymer was found to have a number average molecular weight of 2370, a softening point greater than 360°C. and to be completely soluble in cold benzene. Characterisation of the polymer product by infrared spectroscopy showed a band at 970 cm<sup>-1</sup> indicative of *trans* unsaturation, a band at 1300 cm<sup>-1</sup> indicating *cis* unsaturation and a band at 2120 cm<sup>-1</sup> characteristic of acetylenic linkage. These infrared data indicate a polymer structure having recurring units of:



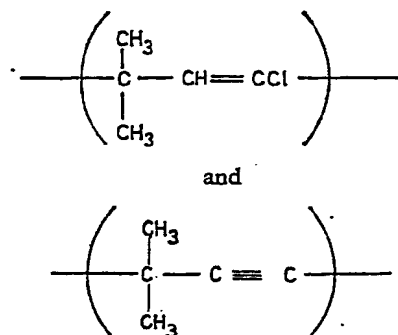
in the polymer chain.

#### EXAMPLE 2

10 ml. of 1,1 - dichloro - 2,2 - dimethylcyclopropane were cooled to -78°C. in an open beaker. 0.25 g. of AlBr<sub>3</sub> in 20 ml. of ethyl chloride was added to the beaker at -78°C. Although a slight turbidity ensued, no reaction was apparent. The reaction was removed from the bath and allowed to warm to room temperature (20°C.) where it was held for 65 hours. A viscous liquid resulted. The reaction mixture was transferred to boiling methanol to dissolve out the catalyst. The viscous liquid polymer was separated from the methanol and dried in a vacuum oven. On characterisation the viscous polymer had a number average molecular weight of 725-731. The polymer product of the present invention has many and varied uses. Such uses include moulded objects where high temperatures will be encountered and inert coatings for acid tanks.

#### WHAT WE CLAIM IS:—

1. A linear polymer containing recurring structural units of the formulae:—



in the polymer chain, and having infrared absorption bands at 970 cm<sup>-1</sup>, 1300 cm<sup>-1</sup> and 2120 cm<sup>-1</sup>.

2. A polymer according to claim 1 which is benzene-soluble and has a softening point greater than 360°C. and a number average molecular weight between 500 and 10,000.

3. A polymer according to claim 1 substantially as hereinbefore described.

4. A polymer according to claim 1, 2 or 3 in solid shaped form.

5. A process for the preparation of the polymer claimed in claim 1, which comprises polymerising 1,1 - dichloro - 2,2 - dimethylcyclopropane in the presence as catalyst of a Friedel-Crafts catalyst at a temperature of 20-100°C.

6. A process according to claim 5 wherein the weight ratio of 1,1 - dichloro - 2,2 - dimethyl - cyclopropane to Friedel-Crafts catalyst is in the range of 100:1 to 1:1.

7. A process according to claim 5 or 6 wherein the polymerisation is effected in the absence of a solvent.

8. A process according to claim 5 or 6 wherein the polymerisation is effected in a solvent which is a saturated hydrocarbon or a chlorinated hydrocarbon.

9. A process for the preparation of a polymer as claimed in claim 1 substantially as hereinbefore described.

10. A polymer as claimed in claim 1 when prepared by a process according to any one of claims 5 to 9.

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